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ARAMIDS WITH CONTROLLED CONSTITUTIONAL ISOMERISM:
SYNTHESIS AND CHARACTERIZATION

W. R. Meyer, F. T. Gentile, and U. W. Suter

Department of Chemical Engineering,
Massachusetts Institute of Technology,
Cambridge, MA 02139

INTRODUCTION

Previously, it has been shown that polycondensates can be synthesized from "non-symmetric" monomers (XabX) and "symmetric" monomers (YccY), giving rise to a constitutional isomerism similar to the "head/tail" isomerism exhibited by vinyl polymers (1,2). This constitutional isomerism in polycondensates can be controlled in a pre-determinable and continuous manner over a wide range of constitutional order. The order parameter, s , is quantified by the probability that two adjacent non-symmetric monomeric units are oriented in the same direction relative to the molecular axis, i.e.

$$s = [accb]/([acca] + [accb] + [bccb])$$

Constitutional isomerism has a profound effect on the properties of polyamides (3,4), partly because more constitutionally regular polyamides yield solids of higher three dimensional order than their more irregular counterparts; packing efficiency and crystallinity are direct functions of order.

In an effort to prepare polymers of controllable structure which possess most of the beneficial properties of poly(p-phenylene-terephthalamide) while having a minimum of the undesirable properties (i.e. poor processibility), the authors have recently synthesized a series of high molecular weight aramids which are analogues of poly(p-phenylene terephthalamide) (PPDT), the non-symmetric monomer being a 2-substituted or 2,6-disubstituted p-phenylenediamine and the symmetric polymer being terephthaloyl dichloride.

MODELLING CONSTITUTIONAL ORDER: FEED RATES V. REACTION RATES

The order parameter is affected by the kinetic mechanisms of the polymerization reactions and the relative mixing of the two monomers (3). Only homo-bifunctional monomers, XabX and YccY, where X and Y are leaving groups and -aX reacts only with -cY and -bX reacts only with -cY are considered.

The kinetic parameters of interest are (i) the ratio of rate constants for the reactions of the functional groups of the non-symmetric monomer XabX, $r = k_{bX}/k_{aX}$ and (ii) the ratio of the reaction rate constant of the second-reacting functional group to that of the first in the symmetric monomer YccY, $g = k_{cY,sec}/k_{cY,first}$. The g parameter must usually be replaced by two different parameters, g_a and g_b , depending on whether the first reacting site has reacted with the aX or the bX site of the non-symmetric monomer.

The relative rates of addition (feed rate) of the two monomers can be chosen in the range from "infinitely" slow to "infinitely" fast addition or any finite value in between. A system of ten first order ordinary non-homogeneous differential equations is solved in order to compute polymer order. Figures 1, 2 and 3 show the dependence of polymer constitution on the rates of addition and the kinetic parameters.

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Figure 1 ORDER V. MONOMER FEED RATES

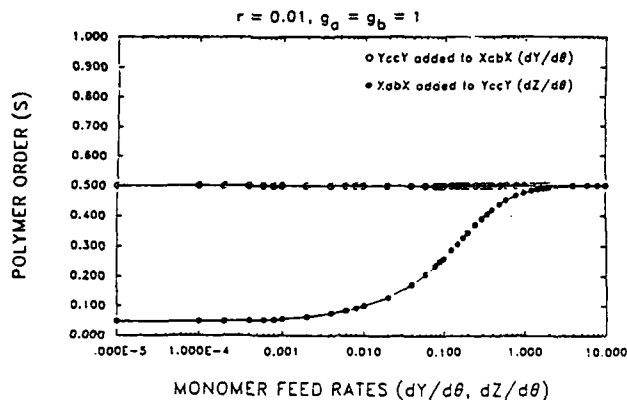


Figure 2

ORDER V. MONOMER FEED RATES

$r = 0.01, g_a = g_b = 0.067$

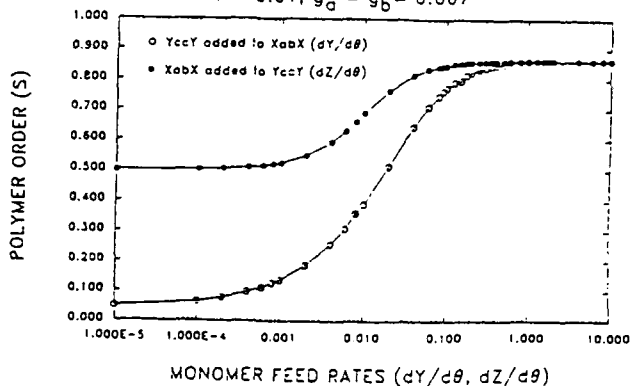
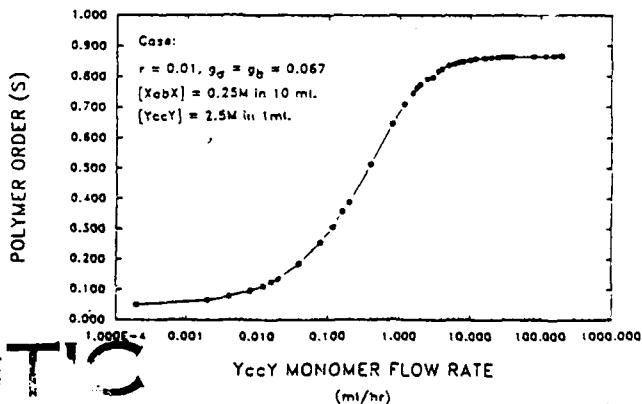


Figure 3

POLYMER ORDER V. YccY MONOMER FLOW RATE



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POLYMERIZATIONS

As monomers, derivatives of p-phenylene diamine (I) and terephthalic acid chloride (II) were used. In order to be able to control the feed rates of the monomers, and thus the constitutional isomerism of the polymers, the reactions must be carried out in homogenous solutions. Polymers of satisfactory molecular weight and controlled regularity were obtained using a modified Schotten-Baumann solution procedure. The choice of an appropriate solvent system is of great importance. Best results were obtained with binary systems composed of tetrahydrofuran (THF) and a cyclical amide such as N-methylpyrrolidone (NMP) with a small amount of lithium chloride (LiCl). The amides were chosen for their solvating power and their ability to bind free protons, while THF was used to solvate the acid chloride, and LiCl keeps the polymers in solution. The role of the solvent will be discussed in detail.

Recently polymers from terephthalic acid chloride (I) and 2,5-diaminopyrimidine were obtained. Their properties and the effect of the constitution on their properties will be discussed.

TABLE I: Examples of Polymers with Controlled Constitutional Structure

I + 2-substituted p-phenylenediamine (II)		
Substituent	Constitution	η_{inh}^a (dl/g)
- NO ₂	ordered	1.67
	random	2.47
- OCH ₃	ordered	1.67
	random	1.72

I + 2,6-substituted p-phenylenediamine (II)		
Substituent	Constitution	η_{inh}^a (dl/g)
- Cl ₂	ordered	1.12
	random	3.54
- OCH ₃	random	0.85

^a "ordered": $s \rightarrow 0$ obtained by very slow addition of non-symmetric diamine to terephthalic acid chloride; "random": $s = 0.5$ obtained by immediate mixing of the monomers.

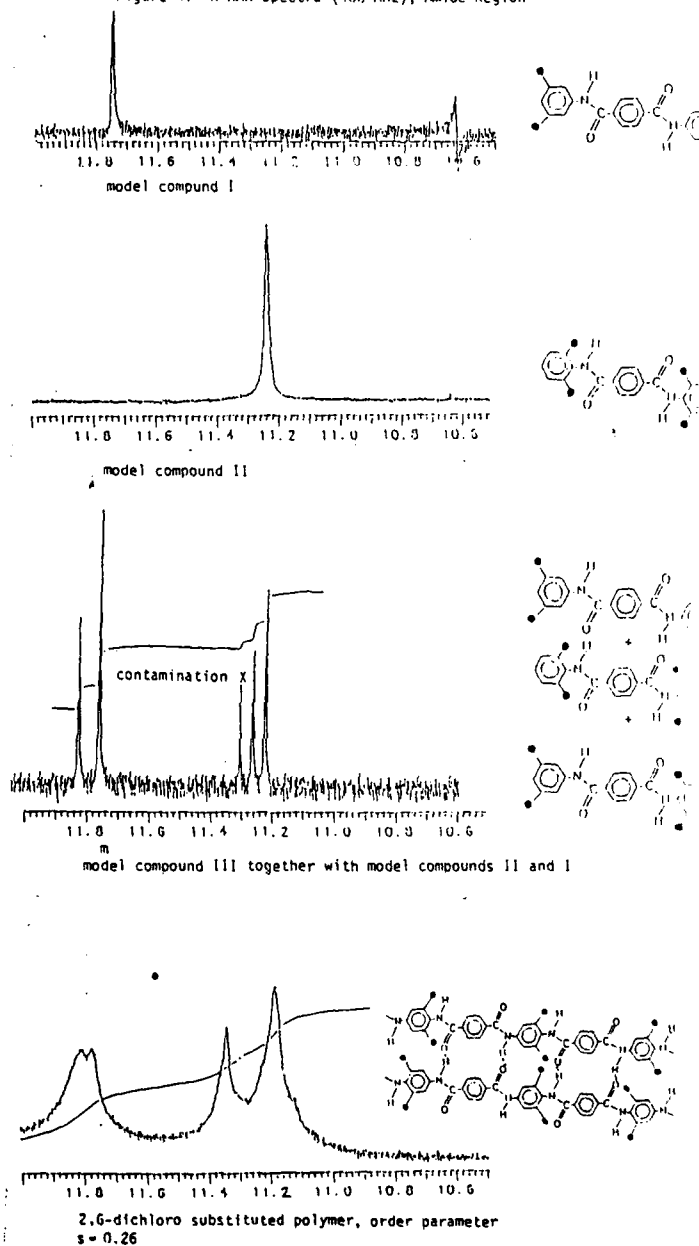
^b measured in 98% sulfuric acid, at a concentration of 0.5 g/dl.

CHARACTERIZATION

The degree of constitutional order has been determined experimentally in some polymers by analysis of the amide proton signal in ¹H NMR spectra. Band assignments were made by comparing the signals in the polymer spectra with the corresponding peaks in the spectra of the three corresponding model compounds obtained by reaction of terephthalic acid chloride with 3,5- and 2,6- disubstituted anilines, respectively. For example, see Figure 4.

The properties of the polymers differ clearly for different constitutional order, s . Polymers with low constitutional regularity ($s \approx 0.5$) show generally much greater solubilities than their more ordered counterparts. Differences in degree of hydrogen bonding in the solid state are being studied using FT-IR spectroscopy.

Figure 4: ¹H NMR Spectra (400 MHz), Amide Region



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